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Spherules associated with the Cretaceous–Paleogene boundary in Poland

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ABSTRACT:

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The succession of the Lechówka section near Chelm in south-eastern Poland presents the first complete record of the Cretaceous–Paleogene (K–Pg) boundary in Poland. Samples of the boundary clay were examined for microtektites and shocked minerals to confirm the impact origin of the sediment. The spheroidal fraction reveals morphological and mineralogical features, e.g., spherules, similar to material from the K–Pg boundary as described from elsewhere. The impact genesis of the spherules is confirmed by the presence of nickel-rich spinel grains on their surfaces. The spinels are considered to be primary microlites and, thus, the spherules at Lechówka can be classified as microkrystites. No shocked minerals were noted. The deposits with spherules comprise Al- and Mg-rich smectite (Cheto smectite). This almost pure Mg-rich smectite, forming up to 100% of the clay fraction, derived from the weathering of the impact glass. It is proposed that the spherules isolated from the Cretaceous–Paleogene boundary clay at Lechówka come from the Chicxulub crater in Mexico.

Key words: Cretaceous–Paleogene boundary; Poland; Spherule; Microkrystites; Impact origin; Ni-rich spinels; Smectite.

INTRODUCTION

Impact melt products ejected from an impact crater as millimetre- to centimetre-sized bodies of pure melt and chilled rapidly to glass, may be deposited hundreds or thousands of kilometres from the impact site as part of a layer of distal ejecta. Altered glass spherules have been identified as tektites or microtektites if they consist of glass without primary microlites (Izett *et al.* 1991; Sigurdsson *et al.* 1991; Blum and Chamberlain 1992; Blum *et al.* 1990; Koeberl 1993) or as microkrystites if they contain primary microlites (Glass and Burns 1988). That microkrystites are usually products of impact vapour condensates may be indicated by

the presence of crystallites of quartz and calcite (Griscom *et al.* 1999). Impact spherules are generally less than 1 mm across.

The formation of millimetre-sized glassy spherules from shock-melted droplets appears to be typical of impact events. Schmidt and Holsapple (1982) estimate that the amount of target rock melted or vapourised by an impact is up to 100 times the mass of the bolide. An amount of target rock over 1000 times the mass of the bolide will show evidence of shock or shock metamorphism (e.g. shatter cones, shock lamellae, stishovite). For every 1 ton of mass in a bolide approximately 15 tons of vapourised, molten and shocked crater material will be ejected into or beyond the atmosphere. Some

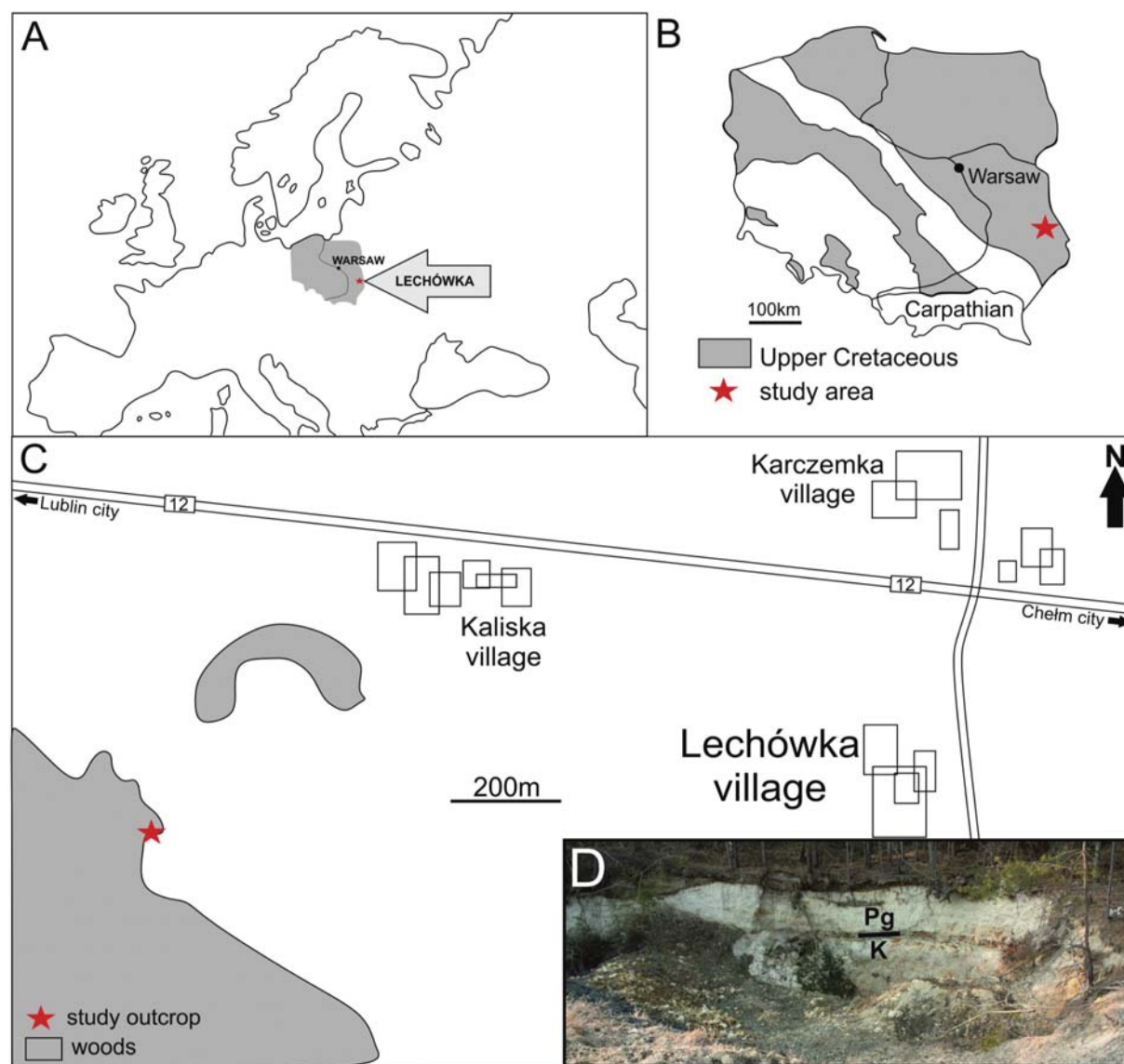
products such as tektites may be ejected at enormous speed (up to 9 km/s) along ballistic trajectories.

The best known and most-studied spherule deposits are from the Cretaceous-Paleogene (K-Pg) boundary layer of distal ejecta from the Chicxulub structure (Mexico). This thin layer is distributed globally from the impact site and contains, as significant components, altered spherules of impact melt (Montanari *et al.* 1983; Sharpton *et al.* 1992; Pollastro and Bohor 1993; Bohor and Glass 1995; references in Sharpton and Ward 1990, Ryder *et al.* 1996).

The discovery of iridium anomalies at the K-Pg boundary led Alvarez *et al.* (1980) to propose meteorite impact as a causal mechanism for mass extinctions at the

end of the Cretaceous. High contents of Ir and platinum-group elements (Ganapathy 1980), the presence of glassy spherules (Smit and Klaver 1981; Izett 1987; Montanari 1991; Kyte *et al.* 1995; Olsson *et al.* 1997; Norris *et al.* 1999), shocked quartz (Bohor and Betterton 1990) and unusual Ni-rich spinels (Kyte and Smit 1986; Robin *et al.* 1991, 1992) at K-Pg boundary sites worldwide, have been attributed to the impact of an asteroid-sized bolide 10 km in diameter. The finding of a piece of the projectile in the North Pacific Ocean (Kyte 1998) indicates that the impactor was a carbonaceous chondrite.

The impact theory (Alvarez *et al.* 1980; Smit and Hertogen 1980) provides a plausible explanation for the



Text-fig. 1. A – Location of the Cretaceous-Paleogene Lechówka section in Poland; B – Upper Cretaceous deposits on a pre-Cenozoic sketch map of Poland (simplified from Voigt *et al.*, 2008, after Pożaryski *et al.* 1979) showing the location of the outcrop at Lechówka; C – Detailed map of the location of Lechówka Quarry; D – General appearance of the outcrop. K – Cretaceous, Pg – Paleogene

majority of mass extinctions at the end of the Cretaceous (Schulte *et al.* 2012). The finding of shocked minerals (Bohor *et al.* 1984) and tektite glass (Sigurdsson *et al.* 1991) supports this hypothesis. Urey (1973) had already predicted that microtektites might be found in deposits due to large impacts. Larger tektites ($\ll 1$ cm) have been occasionally reported (Smit 1999). Spherules are usually restricted to the thin impact layer (Smit *et al.* 1992).

Racki *et al.* (2011) discovered the first complete record of marine K–Pg boundary deposits in Poland, at the Lechówka Quarry in the south-eastern part of the country. They reported anomalously high amounts of iridium and other siderophile elements in the strata, consistent with a chondrite meteoritic composition and the Chicxulub impact. Mineralogical, as well as geochemical studies presented in this paper confirm the impact origin of the K–Pg boundary clay in Lechówka, as proposed by Racki *et al.* (2011).

The main aim of this study was to search for shocked minerals and microtektites in the boundary clay at Lechówka which could provide geological evidence of the end-Cretaceous impact. This had been impossible earlier due to the presence of stratigraphic gaps at the K–Pg boundary in other Polish sections (Hansen *et al.* 1989; Machalski 1998).

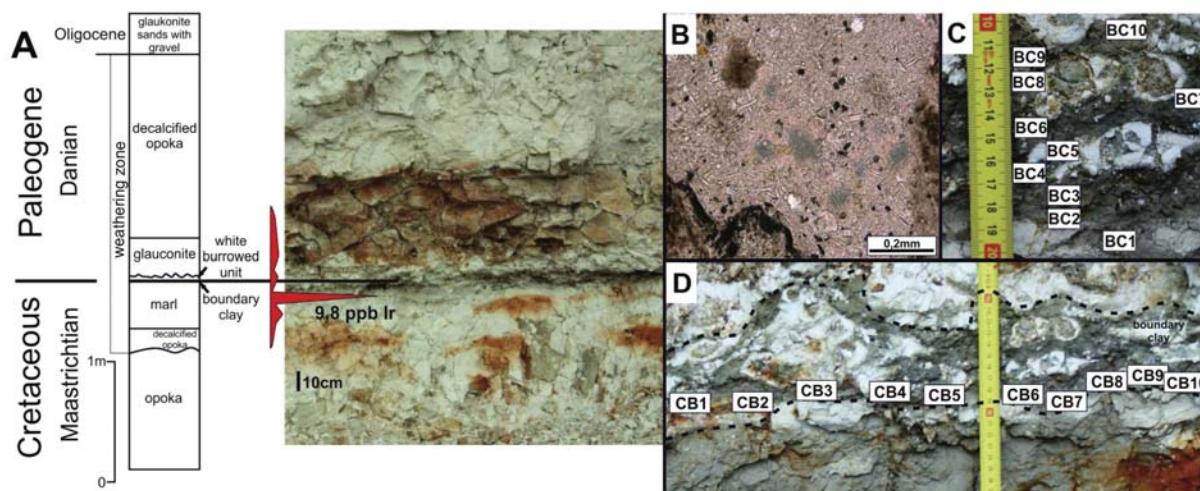
GEOLOGICAL SETTING

The Lechówka Quarry is situated between the cities of Lublin and Chełm in eastern Poland, near the Polish-Ukrainian border (Text-fig 1A, B and C). Palaeogeographically, this was the eastern part of the Danish–Polish Basin (Ziegler 1990). The section in the quarry is c.

4 m deep and c. 20 m long (Text-fig 1D).

In their description of the Lechówka section, Racki *et al.* (2011) identified eight depositional units; six of them are reported herein. The two lowest units (10 cm thick opoka and a 70 cm thick tectonic/karstic breccia units) are not currently exposed. Based on Racki *et al.* (2011), the exposed part of the Lechówka succession is as follows (in stratigraphic order) (Text-fig 2A):

- 100 cm thick opoka layer with an undulating decalcified top which passes into the overlying sediments;
- c. 35 cm thick marly layer with bioturbation at the top. The chemostratigraphic profile by Racki *et al.* (2011) shows that the highest concentration of iridium (9.8 ppb) is found in this horizon, c. 10 cm below the boundary clay (Text-fig 2A). Racki *et al.* (2011) explain this as due to intensive circulating of humic, acid-rich ground waters during long-lasting Paleogene weathering under humid conditions, also responsible for the pronounced decalcification;
- c. 10 cm thick clay layer with a rusty base with burrows and decalcified opoka clasts. Unidentified microfauna is presented in the top clay layer (Text-fig 2B). The accumulated microfauna is a characteristic feature of the lowest Danian deposits in studied profile;
- c. 12–15 cm white burrowed unit, consisting of decalcified rock clasts with burrows at the base. The burrows are filled with glauconite, the content of which increases upwards;
- c. 40 cm glauconite layer with white opoka clasts;
- c. 150 cm thick decalcified opoka layer with clasts of flint remnants of original limestone intercalations, comparable to similar deposits in the so-called Siwak succession in the Middle Vistula section (Racki *et al.* 2011; see also Hansen *et al.* 1989 and Machalski 1998).



Text-fig. 2. A – Stratigraphy and lithological profile from the Lechówka quarry with location of the marked iridium peak noted by Racki *et al.* (2011); B – unidentified microfauna of earliest Danian age in the upmost boundary clay; C – location of boundary clay sampling in November 2011; D – location of boundary clay sampling in August 2012 of the spherule-bearing layer at Lechówka

The Cretaceous succession at Lechówka is overlain by a 50 cm thick layer of glauconite sand with gravel, ascribed conventionally to the Oligocene.

SAMPLES AND METHODS

Ten samples with a total weight of 5 kg were collected from the c. 10 cm thick boundary clay (Text-fig 2C). Subsequently, a further 10 samples with a total weight of 5 kg, were collected (Text-fig 2D). A thin section of the K–Pg boundary clay failed during polishing, due to the water used in the procedure. The clay minerals were totally washed out. Every sample from the boundary clay deposits was remaindered on sieves (mesh 63 μm). The separated fraction was investigated using a Philips XL 30 ESEM/TMP scanning electron microscope (SEM) equipped with an EDS (EDAX) detector. X-ray analyses (XRD) of the boundary clay with spherules were undertaken using a Panatytical X'Pert PRO MPD PW 3040/60 equipped with Theta-Theta geometry. The analyses were carried out at the Faculty of Earth Science in the University of Silesia, Sosnowiec.

RESULTS

Examination of the first 10 samples revealed the presence of spherules in two of them (samples BC2 and BC3; Text-fig 2C). The SEM investigation revealed the presence of spherules in all of the latter (Text-fig 3A). The spherules come from the base of the boundary clay. They range from 200 to 300 μm in diameter. A Ni-rich spinel (magnetite?) grain was found on the surface of one spherule. No shocked minerals were noted in the boundary clay.

The XRD analysis showed that the boundary clay is composed of smectite, mainly nontronite, and montmorillonite. These clay minerals occur with white mica, kaolinite, silica, quartz, sanidine, phosphates and, as accessories, augite and diopside crystals.

DISCUSSION

Microtektites are formed by the impact-melting of silica-rich rocks. Most impact spherules are generated during the first stages of crater formation when melted rocks are ejected. However, K–Pg spherules with Ni-rich spinels, which may have been produced as condensate droplets from an impact plume, appear to be mi-

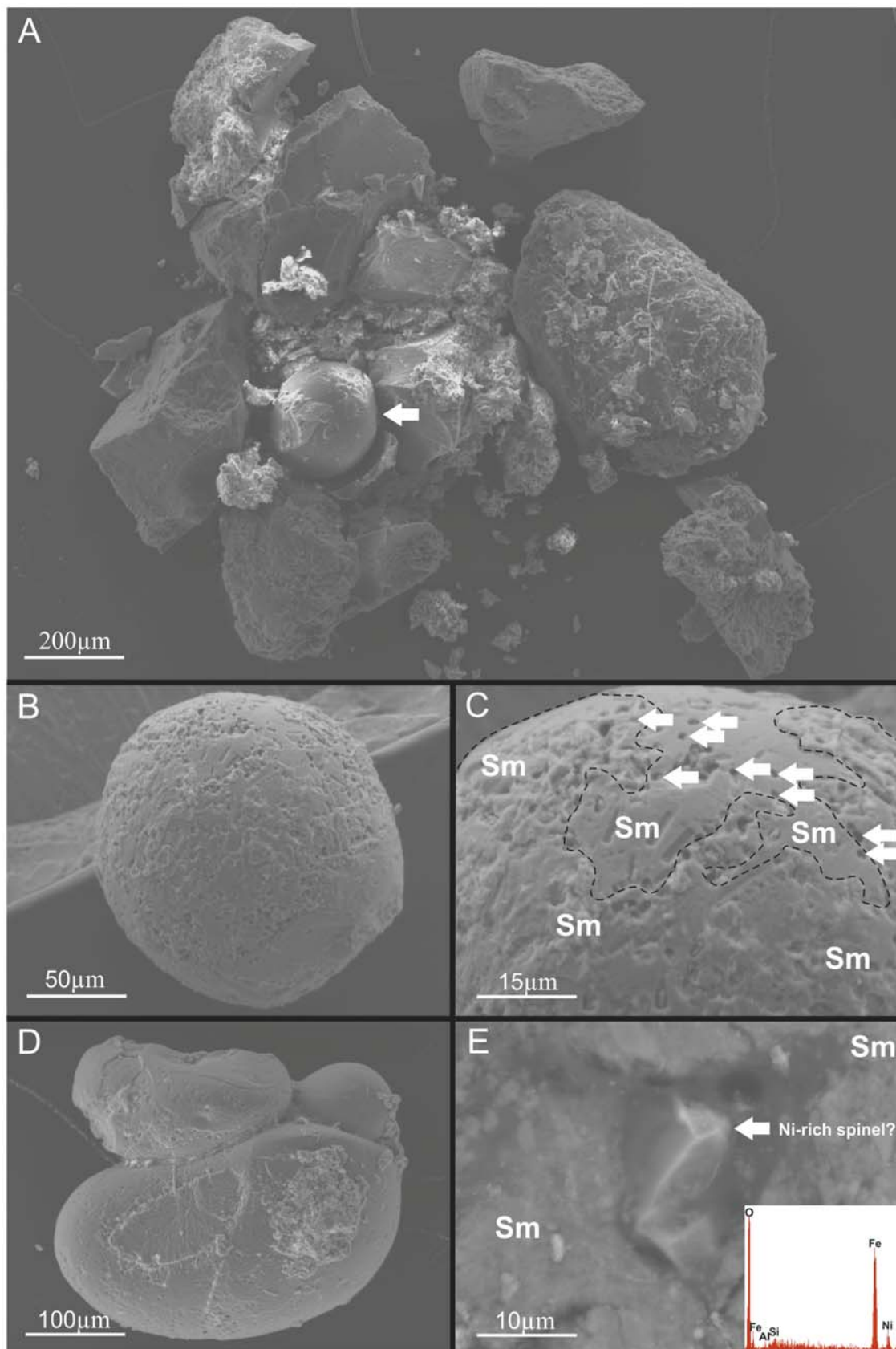
crokrystites. Glass and Simonson (2013) proposed that these droplets are formed as a result of the vapourisation of mafic components during the impact and related melting. Many workers, however, think that vapourisation of the bolide contributes a lot to the mafic composition of the distal spherules (see discussion in Glass and Simonson 2013).

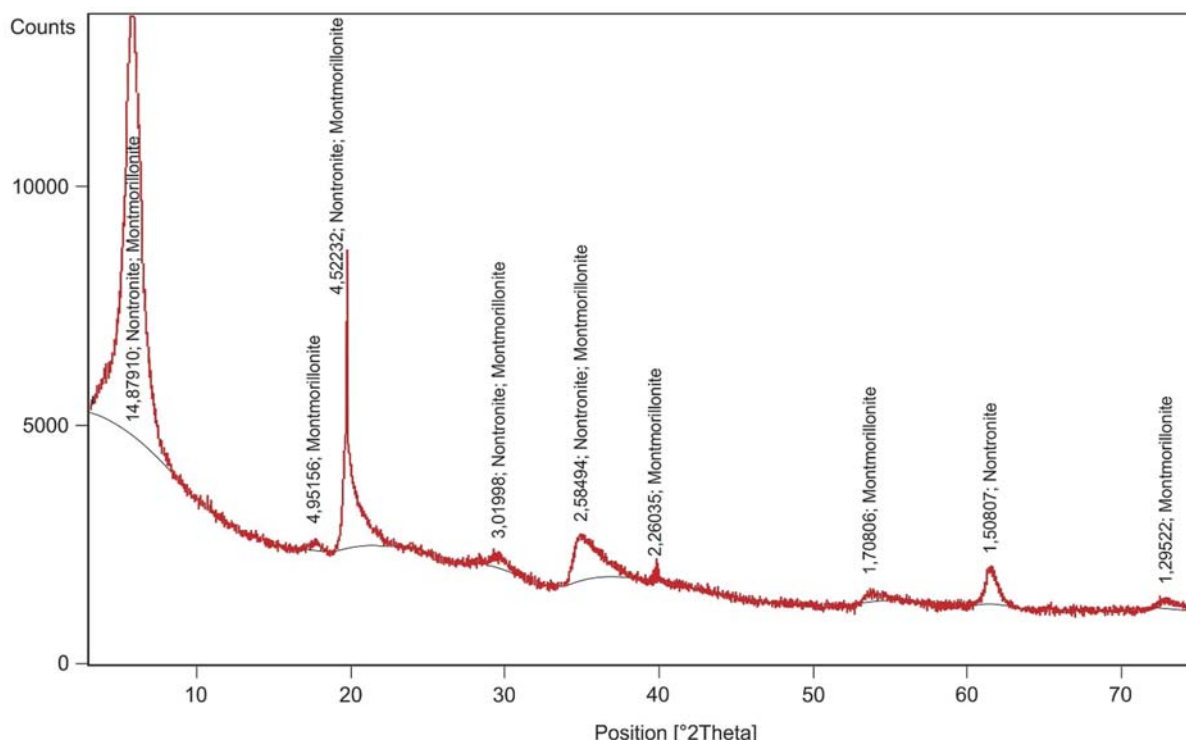
The major mineral phase in most impact spherules is glass, which is usually replaced by other phases, i.e., smectite, glauconite, K-feldspar, calcite or quartz, in deposits older than Cenozoic (Glass and Simonson 2013). Montmorillonite and nontronite are the main minerals of both the Lechówka boundary clay and its spherules. Ni-rich spinel grains with high nickel contents and high ferric ratios indicate highly oxidizing conditions during crystallization in the atmosphere (Robin *et al.* 1992).

Microtektites generally exhibit a variety of surface features including pits or grooves. In contrast, K–Pg spherules are generally smooth although their surfaces may show sculpturing (Bohor and Betterton 1990; Sigurdsson *et al.* 1991) and altered phases. Small, regular, internal cavities were probably originally gas bubbles (Klaver *et al.* 1986) or microspherules (Glass and Simonson 2013; Text-fig 3B). All of the Lechówka spherules seen appear to be spherical. Teardrop- or disc-like shapes have not been observed, but there are numerous examples composed of two or more probably distorted spherules that fused together (Text-fig 3C) – as was noted by Glass and Simonson (2013). All of the spherules occur in the lower part of the K–Pg boundary clay. The fact that spherules occur only in the lower part of the boundary clay at Lechówka, i.e., the layer defined by samples BC2 and BC3 (Text-fig. 2C), is consistent with the fact that, as Bohor and Betterton (1990) pointed out, these occur in the lower part of the K–Pg boundary clay everywhere.

Ni-rich spinels. Ni-rich spinel crystals are globally distributed in K-Pg boundary deposits where they generally occur on altered spherules (Kyte and Smit 1986; Bohor *et al.* 1986). They have also been found in Precambrian- and Late Eocene spherules (Glass and Simonson 2013). The Ni-rich spinels have been recognized as magnetites by Montanari *et al.* (1983), as spinels by Kyte and Smit (1986) and as magnesioferrites by Bohor *et al.* (1986). They range in size from <5 μm up to 50 μm (Bohor *et al.* 1986; Kyte *et al.* 1995). Ni-rich impact spinels generally occur as subhedral to euhedral forms, frequently skeletal, and as dendritic forms or octahedral crystals (Bohor *et al.*

Text-fig. 3. A – One of the spherules found at the base of the boundary clay at Lechówka; B – Detail of spherule surface with a thin, characteristic coating of smectite (Sm); C – Arrows indicate small and regular cavities; D – Cluster of what are probably three distorted spherules; E – probable Ni-rich spinel as suggested by EDS spectrum





Text-fig. 4. X-ray diffraction pattern of spherule from Lechówka

1986; Kyte *et al.* 1996). These kinds of morphologies indicate rapid crystallization and cooling from a high-temperature melt (Bohor *et al.* 1986; Kyte *et al.* 1995). Although Kyte and Bohor (1995) and Glass and Simonson (2013) illustrated Ni-rich magnesioferrite spinels recovered from K–Pg impact boundary sediments, Ni-rich spinels are not, by themselves, an adequate proof of impact shock nor an explanation for the origin of spherules. However, their occurrence in spherules does indicate meteoritic contamination (Glass and Simonson 2013). After consultation with Prof. B. Glass, it seemed that Ni-rich spinels might occur on the surface of some spherules from Lechówka, as confirmed by crystallographic form and elemental composition (Text-fig 3D).

Spherule composition. Smectite spherules from the K–Pg boundary have been described by Izett (1987, 1990) among others. Sometimes, spherules may be surrounded by a very thick cover of smectite that has a different form from the mantle. A similar situation is observed in the Lechówka spherules. All of the spherules are made of smectite. These are coated by thin mantles of smectite (Text-fig. 3B) similarly as noted by Izett *et al.* (1991) in Haitian spherules. Klaver *et al.* (1986) reported spherules completely altered to smectite from a few boreholes in the North Atlantic. An

impact origin for smectite spherules was confirmed by Sigurdsson *et al.* (1991) and Bohor and Glass (1995). Spherules altered diagenetically to smectite have also been described by Martínez-Ruiz *et al.* (2001).

The composition of the spherules from Lechówka and some other sections are given in Table 1. The Lechówka spherules have the highest Al_2O_3 content of all those shown, which may indicate the highest content of smectite (Text-fig 4). Based on their major-element composition, the Lechówka spherules are very similar to the K–Pg boundary clay as exposed at Stevns Klint, Denmark albeit, except Al_2O_3 , the oxide content is lower. Additionally, the spherules lack TiO_2 . Smectite is also the predominant mineral in the Danish K–Pg deposits. Kastner *et al.* (1984) have ascribed similarities between smectite in the ambient clay of the layer and that from meteorite impact glass in the same sediment complex to the same origin. Spherules from sections described by Glass *et al.* (2004) have slightly greater TiO_2 contents compared to those from Lechówka, and tektite glasses from Mexico and Haiti have smaller MgO contents. In smectite-rich areas of the Lechówka boundary clay, smectite occurs as thin ribbon-like packets that form intricate patterns. The packets are curved and have a diverse morphology. According to Li *et al.* (1997), similar features are typical of the complete alteration of glass shards to smectite.

	Lechówka ^a (Poland)	Stevns Klint ^b (Denmark)	Caribbean Sea, Gulf of Mexico, Pacific and Indian Oceans sites ^c (average)	Mimbral ^d (Mexico)	Beloc ^d (Haiti)
SiO ₂	62.58	64.42	64.8	62.99	63.09
Al ₂ O ₃	22.96	18.54	7.42	15.73	15.21
MgO	4.67	6.22	7.37	3.01	2.74
FeO	3.47	3.83	7.18	5.32	5.44
CaO	4.47	5.99	9.91	6.88	7.26
Na ₂ O	0.16	0.22	0.89	3.34	3.63
K ₂ O	0.6	0.79	1.85	0.7	0.67
TiO ₂	0.4	-	0.31	0.7	0.67

^athis study; ^bBauluz *et al.* (2000); ^cGlass *et al.* (2004); ^dSmit *et al.* (1992).

Table 1. Chemical composition (wt%) of spherules from Lechówka, Stevns Klint, Caribbean Sea, etc. and tektite glasses (Mimbral and Beloc).

Spherule deposits can be composed of Al and Mg-rich smectite (Cheto smectite) as evidenced by the high contents of these elements (Table 1). Cheto smectite is an almost pure high-Mg smectite that may form < 100% of the clay fractions derived from the weathering of impact glass, i.e., melt rock and vapour condensates (Debrabant *et al.* 1999; Bauluz *et al.* 2000). Debrabant *et al.* (1999) observed Cheto smectite in altered impact-glass spherule deposits of El Caribe in Guatemala and Ceibo in Central Mexico, and Bauluz *et al.* (2000) noted this smectite in the boundary clay at Stevns Klint. According to Smit *et al.* (1992), the high Ca content in K–Pg spherules reflects the presence of carbonate rocks in the basement, where the impact occurred.

Spherule origin. Naslund *et al.* (1986) believed that the K–Pg spherules had a volcanic origin, and reported spherules from other clay layers above and below the K–Pg boundary in the Gubbio section in Italy and in Caravaca, Spain. Others have also proposed a volcanic origin for the K–Pg spherules (e.g., Officer and Lyons 1993). Volcanic spherules are spherical because of the very low gas-content of the mafic lavas and all occur close to the eruptive vents. Mafic spherules from the K–Pg boundary occur > 2000 km from the nearest volcanic source, making it hard to ascribe such occurrences to a non-violent eruption. Although highly improbable, an extremely violent volcanic eruption might lead to spherule transport over large distances. Violent eruptions, driven by high gas pressures, result in tephra that are not spherical but angular shard- and

blade-like in shape (Smit 1990). Vesicles can occur in splash-formed volcanic spherules but are absent on mikrokrytites formed as condensate droplets (Glass and Simonson 2013). The strong geochemical anomaly (see Racki *et al.* 2011) associated with spherule layers also supports the impact origin. Though most researchers accept an impact origin for most K–Pg spherules, some have proposed other kinds of origin, e.g., biogenic (Hansen *et al.* 1986) and authigenic (Izett 1990).

Source of spherules. Assuming that the Lechówka spherules have an impact origin, consideration that the Chicxulub crater may be their source is merited. Data for the Cenozoic microtektite layers indicate that microtektites can be found out to 280 transient crater diameters (Glass and Simonson 2013). Thus, microtektites from Chicxulub can be expected all over the earth ($180 \text{ km} \times 280 = 50400 \text{ km}$). Altered microtektites from the K–Pg boundary have been reported in North Pacific cores (Kyte *et al.* 1996), in Europe and Asia (Republic of Georgia; Smit 1999) at distances up to < 10000 km, i.e., c. 53 crater diameters from Chicxulub. Based on this reasoning, the Lechówka spherules could easily have derived from the Chicxulub impact structure.

CONCLUSIONS

The occurrence of spherules in a layer within slowly-deposited sediment suggests a sudden and catastrophic

event (Hassler and Simonson 2001; Simonson 2003). Generally, impact spherules, without evidence of crystalline textures and which do not contain spinel crystals, are probably microtektites (Glass and Simonson 2013). Thus, the spherules from the Lechówka section are microkrystites. The identification of impact spherules is problematic, especially if the spherules have been diagenetically altered. Moreover, no boundary layer is known that contains evidence of shock metamorphism, e.g., shocked quartz. Nonetheless, spherules acting as the precursor of smectite, with shapes, sizes and chemical compositions similar to spherules described from elsewhere on the Earth, and characterized by an Ir anomaly and Ni-rich spinels, serve to indicate an impact origin for the K–Pg boundary clay at Lechówka, as proposed by Racki *et al.* (2011).

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